# Environmentally Benign Pyrotechnic Delays

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## ABSTRACT

Pyrotechnic delays are used in commercial and military items requiring a time delay between two energetic events. For example, US Army hand-held signals (HHS) use a delay element to properly sequence the expulsion of illuminating rounds at the rockets' apex. Many military delay formulations contain barium, lead, chromates, and perchlorates. The US Army is reformulating pyrotechnic items to remove environmentally hazardous materials. In this paper, new environmentally benign formulations are described. The delay time of the new system is easily tunable. These compositions will consistently function in aluminum housings which is generally difficult for delay compositions due to extreme thermal losses that can cause quenching.

## Introduction

Pyrotechnic delays have long been used by the military to provide a reproducible time interval between two energetic events. For example, in the M125A1 hand-held signal, the soldier activates the rocket by striking the primer which ignites the propellant that propels the rocket. The delay column is simultaneously lit, thus providing a timed interval allowing the rocket to reach apogee before the expulsion charge expels green light-emitting pyrotechnic clusters. Until the mid-20$^{th}$ century, black powder was the material of choice for delays [1, 2]. Black powder delays can provide very reproducible intervals, but they must be vented due to the large amount of permanent gas generated during combustion. The development of gasless delays (generating 5-10 mL/g of gas or less) enabled sealed fuzes and more sophisticated munitions.

Modern pyrotechnic delays are composed of a metallic or semi-metallic fuel, chromate and/or perchlorate-based oxidizers, and a diluent or binder. The traditional tungsten delay, MIL-T-23132A, contains tungsten (fuel), barium chromate (main oxidizer), potassium perchlorate (secondary oxidizer), and diatomaceous earth (diluent). The variant used in the hand-held signal delay element contains VAAR, and no diluent. The chromate and perchlorate oxidizers are being targeted by the United States Department of Defense for removal from pyrotechnic formulations due to environmental regulation. In 1997, the Army National Guard in Massachusetts halted use of the M115/116 flash bang simulator at Camp Edwards due to ground water contamination attributed to perchlorate residue from these items. The Pyrotechnics Division of the US Army Armaments Research, Development, and Engineering Center (ARDEC) reformulated these devices and in 2010 the M115/116 was used at Camp Edwards for the first time in 13 years [3]. The Pyrotechnics Division is now developing environmentally benign delay formulations, which may be used in many different munitions, to help ensure that the Nation's warfighters will be able to effectively train with these items.

What makes a good delay formulation? Delays need to be reliable, easy to manufacture, able to function in different housings, and easy to ignite. Ideally, they should be gasless, and the system should be tunable. Gasless delays benefit from minimal changes in performance as altitude varies, and may also

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14. ABSTRACT

**Pyrotechnic delays are used in commercial and military items requiring a time delay between two energetic events. For example, US Army hand-held signals (HHS) use a delay element to properly sequence the expulsion of illuminating rounds at the rockets apex. Many military delay formulations contain barium, lead, chromates, and perchlorates. The US Army is reformulating pyrotechnic items to remove environmentally hazardous materials. In this paper, new environmentally benign formulations are described. The delay time of the new system is easily tunable. These compositions will consistently function in aluminum housings which is generally difficult for delay compositions due to extreme thermal losses that can cause quenching.**

15. SUBJECT TERMS

**delay, pyrotechnic, fuze, hand-held signal, environmental**

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be used in sealed housings. A tunable system allows the same base components to be used for a variety of desired burn rates. In this study, a novel gasless ternary system consisting of silicon, bismuth(III) oxide, and antimony(III) oxide is described. The compositions give reliable time intervals, are readily prepared by simple dry mixing techniques, and are able to function in aluminum or stainless steel housings. They are also easily ignited by black powder, a relatively low-temperature igniter which is especially convenient for testing purposes. The effect of changing the oxide ratio and the housing material on burn rates is discussed.

## Experimental

**Materials:** Silicon (MIL-S-230, grade 2, class C) was obtained from AEE. Bismuth(III) oxide ($Bi_2O_3$) and antimony(III) oxide ($Sb_2O_3$) were obtained from Alfa Aesar. A Malvern Morphologi G3S optical microscopy particle size analyzer was used to determine number-based CE (circle-equivalent) diameter distributions. Volume-based distributions were calculated. The data are presented in Table 1.

**Table 1. Particle size data (μm).**

| Material | Data | CE Diameter Mean | D[n, 0.1] | D[n, 0.5] | D[n, 0.9] |
|---|---|---|---|---|---|
| Si | number-based | 3.82 | 0.98 | 2.74 | 7.80 |
| $Bi_2O_3$ | number-based | 6.59 | 2.36 | 5.60 | 11.73 |
| $Sb_2O_3$ | number-based | 5.39 | 1.68 | 4.17 | 10.05 |

| Material | Data | D[4,3] | D[v, 0.1] | D[v, 0.5] | D[v, 0.9] |
|---|---|---|---|---|---|
| Si | volume-based | 25.46 | 6.27 | 15.69 | 49.69 |
| $Bi_2O_3$ | volume-based | 36.37 | 7.45 | 15.71 | 87.65 |
| $Sb_2O_3$ | volume-based | 57.86 | 9.15 | 35.47 | 126.90 |

D[4,3] is the volume mean diameter.
D[n, 0.1] is the diameter at which 10% of the number distribution is below.
D[v, 0.1] is the diameter at which 10% of the volume distribution is below.

**Mixing:** The compositions are dry mixtures of two or three components. To prepare each composition, the materials were combined in a small conductive container and the following procedure was followed:

1. vibrational mixing for one minute
2. pass through 50 mesh screen
3. vibrational mixing for one minute
4. pass through 50 mesh screen
5. vibrational mixing for one minute

A Scientific Industries Vortex-Genie was used for the vibrational mixing steps. The screening steps were necessary to break up clumps. The procedure gave delay mixes with reliable and reproducible performance.

**Loading:** Aluminum (2024-T3) or stainless steel (304L) tubes were used as delay housings. These tubes had an inner diameter, outer diameter, and length of 0.48 cm, 0.95 cm, and 1.52 cm,

respectively. Black powder (class 7, 40-100 mesh) was used for the input and output charges. Pressing was performed with a Carver hydraulic press. Each housing was placed in a tooling die and then the following procedure was followed:

1. add 0.050 grams black powder and lightly tamp
2. add 0.250 grams delay composition
3. press
4. add 0.250 grams delay composition and lightly tamp
5. add 0.050 grams black powder
6. press

The pressing steps were done at 340 kg dead load with a 10 second dwell time. This corresponds to 188 MPa. Pressed in this way, the input and output charges (the black powder) collectively occupied approximately 0.30 cm. Depending on the composition density, the total column length varied from 1.09 cm to 1.20 cm. The tooling die was configured so that there was a fixed 0.16 cm indentation from one end of the tube to the start of the column. This centered the longer columns in the tubes, while the shorter ones were slightly offset.

**Measurements:** The delay columns were ignited with a 2.5 cm V-shaped piece of 20-gauge nichrome wire, heated by a TDK Lambda GEN 750 power supply. The burn times were measured with a Vision Research V7 high speed video camera with a Nikon 20-80 mm camera lens at a frame rate of 100 frames per second. The camera was manually triggered prior to igniting the column. The burn time was determined by calculating the time difference between the second frame of visible ignition that occurred at the top (input) and bottom (output) of the column. For each composition and housing combination, five tubes were tested and the results were averaged. Inverse burn rates (s/cm) were calculated by dividing the burn times by the length of the delay columns. The entire column length (including the black powder input and output charges) was used in these calculations.

## Results and Discussion

Table 2 and Figure 1 show the inverse burn rates in both 2024-T3 aluminum and 304L stainless steel tubes. In this study, the silicon fuel level was held constant at 30% while the $Bi_2O_3/Sb_2O_3$ ratio was varied. $Sb_2O_3$ was varied from 0-25% as $Bi_2O_3$ varied from 70-45%. As the $Sb_2O_3$ content increased, the inverse burn rates increased over 3-fold, from 0.54 to 1.82 s/cm in aluminum tubes and from 0.68 to 2.25 s/cm in stainless steel tubes. Partial propagation was observed for the composition containing 25% $Sb_2O_3$. In this case, 3/5 aluminum tube items functioned properly, allowing an average time to be determined. All five stainless steel tubes containing this composition failed to propagate completely.

**Table 2. Average inverse burn rate for each composition in aluminum and stainless steel tubes. Note that PP indicates partial propagation. (Standard deviations in parentheses.)**

| Formulation (Si / $Bi_2O_3$ / $Sb_2O_3$) | Aluminum Tubes (s/cm) | Stainless Steel Tubes (s/cm) |
|---|---|---|
| 30 / 70 / 0 | 0.54 (0.0061) | 0.68 (0.073) |
| 30 / 65 / 5 | 0.74 (0.053) | 0.92 (0.077) |
| 30 / 60 / 10 | 0.91 (0.012) | 1.12 (0.079) |
| 30 / 55 / 15 | 1.04 (0.051) | 1.51 (0.10) |
| 30 / 50 / 20 | 1.41 (0.12) | 2.25 (0.13) |
| 30 / 45 / 25 | 1.82 (0.22) | PP |

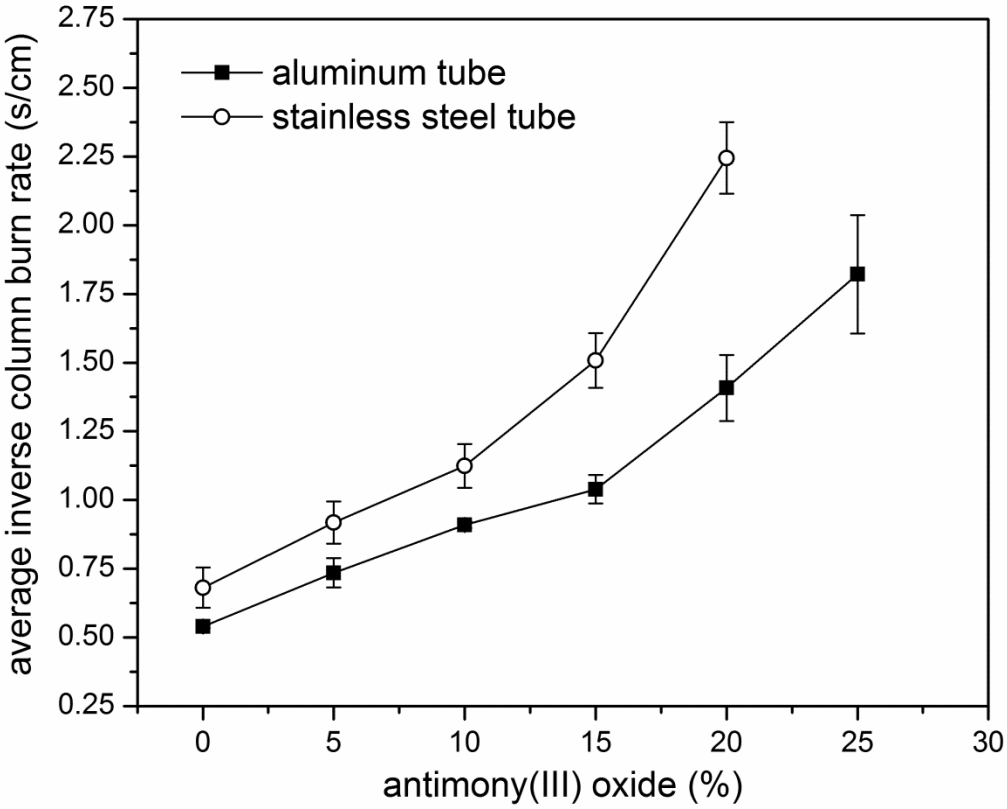


**Figure 1. Average inverse burn rate vs. weight percent of $Sb_2O_3$.**
**Note that the error bars represent a total of two standard deviations for each point.**

In Figure 2, a series of images is shown from the video file of a 30% Si, 55% $Bi_2O_3$, 15% $Sb_2O_3$ composition tested in an aluminum tube. Frame (a) shows the nichrome wire glowing as current is applied, just prior to igniting the black powder input (frame b). As the black powder ignites, it produces a bright flame indicating the start of the burn time (frame c). Flame is emitted as the black powder input is consumed (frame d). As the column continues to burn, a thin visible smoke emanates from the top of the tube (frames e, f). This shows the nearly gasless combustion of the mixed-oxide formulation. Finally, the burning composition ignites the black powder charge on the opposite end of the tube and a flame is seen exiting the bottom (frames g, h). The final time is taken from the second frame of flame emitted from the bottom of the delay column (frame h).

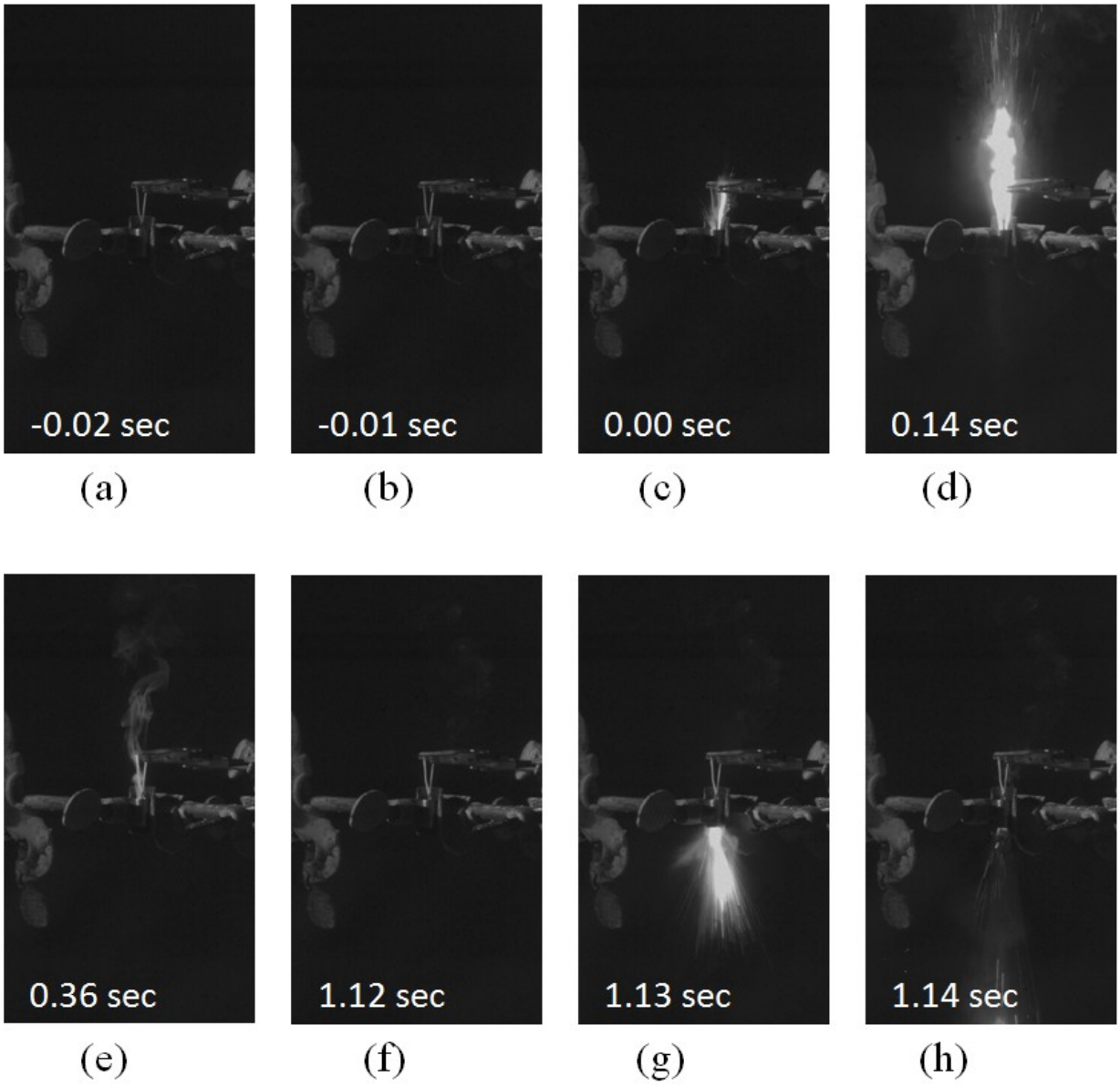


**Figure 2. A series of images taken from video of the 30% Si, 55% $Bi_2O_3$, 15% $Sb_2O_3$ composition tested in an aluminum tube. The burn time starts at frame c and ends at frame h.**

Several authors have reported data for the burn times of binary Si/$Bi_2O_3$ and Si/$Sb_2O_3$ systems. Brammer reported an inverse rate of 0.26 s/cm for a 30/70 Si/$Bi_2O_3$ composition in lead tubes [4]. For 30/70 Si/$Sb_2O_3$, Rugunanan and coworkers measured an inverse rate of 1.59 s/cm for mixes pressed in stainless steel tubes [5]. It is clear from the literature that Si/$Bi_2O_3$ and Si/$Sb_2O_3$ mixtures have very different burn rates. Work reported by Rugunanan [6] demonstrated that ternary systems, such as Si/$Sb_2O_3$/$KNO_3$, could be used as slow-burning delay compositions. The preliminary data we report in this study shows that it is possible to tune burn rate by varying the $Bi_2O_3$/$Sb_2O_3$ ratio in the Si/$Bi_2O_3$/$Sb_2O_3$ ternary system. The compositions emit little gas as evidenced by minimal smoke observed during delay time measurements. When one considers the possible combustion products of this ternary system it is easy to reason that permanent gases are unlikely to form.

The delay housing material also plays a major role in controlling the burn rate of a mix. Several studies describe the effect of different tube materials (e.g. aluminum and lead) on the observed burn rates. Two parameters that greatly influence the heat transfer from the mix to the tube are the thermal effusivity ($e$) and thermal diffusivity ($\alpha$). The equations for both the thermal effusivity and thermal diffusivity are calculated from the density ($\rho$), specific heat capacity ($c_p$), and thermal conductivity ($\lambda$), and are given below:

$$e = \sqrt{\lambda \rho c_p}$$

$$\alpha = \frac{\lambda}{\rho c_p}$$

The thermal effusivity is a measure of a material's ability to exchange thermal energy with its surrounds, while the thermal diffusivity is a measure of how fast the material's temperature adapts to its surroundings. Table 3 shows the values of thermal effusivity and thermal diffusivity for different metals and the tube materials used in this study.

**Table 3. Densities and thermal properties of materials.**

| Material | $\rho$ | $c_p$ | $\lambda$ | $e$ | $\alpha$ |
|---|---|---|---|---|---|
| | $kg \cdot m^{-3}$ | $J \cdot kg^{-1} \cdot K^{-1}$ | $W \cdot m^{-1} \cdot K^{-1}$ | $W \cdot s^{1/2} \cdot m^{-2} \cdot K^{-1}$ | $m^2 \cdot s^{-1}$ |
| Cu (pure) | 8930 | 385 | 398 | 36991 | $1.16 \times 10^{-4}$ |
| Al (pure) | 2700 | 900 | 210 | 22590 | $8.64 \times 10^{-5}$ |
| Si (pure) | 2329 | 713 | 124 | 14350 | $7.47 \times 10^{-5}$ |
| Pb (pure) | 11350 | 129 | 33 | 6951 | $2.25 \times 10^{-5}$ |
| Al alloy 2024-T3 | 2780 | 875 | 121 | 17156 | $4.97 \times 10^{-5}$ |
| stainless steel 304L | 8030 | 500 | 16 | 8015 | $3.99 \times 10^{-6}$ |
| | Data obtained from MatWeb (www.matweb.com). | | | | |

In this study, the compositions pressed in stainless steel tubes had significantly *longer* burn times than those pressed in aluminum tubes, which is contrary to findings reported by other groups. Swanepoel and coworkers studied Mn as a fuel with various oxidizers in lead and aluminum tubes. Several of their systems were quenched in aluminum tubes, and only $Mn/Cu_2O$ propagated reliably at slow rates in this tube material [7]. Kalombo and coworkers observed that $Si/Bi_2O_3$ and $Si/Sb_6O_{13}$ mixtures burned faster in lead tubes than in aluminum tubes [8]. They attributed this effect to the higher thermal conductivity of aluminum compared to lead. Aluminum's thermal conductivity is six times greater than that of lead. Heat transfer from the mix to the tube is greater with the aluminum tubes, leading to a reduction in reaction temperature and a reduction in burn rate. In addition to tube material, the tube length, inner diameter, and outer diameter can have a large effect on delay performance. Changes in the surface/volume ratio of the tubes can influence burn rate, or even quench the reactions in some cases.

So the question remains: Why did the compositions in *this* study show faster rates in aluminum tubes than in stainless steel tubes? Since aluminum has both higher thermal effusivity and thermal diffusivity than stainless steel, the heat generated by the reaction, and consequently transferred to the inner walls of the tube, is transmitted more rapidly down the walls in the aluminum tubes. It is hypothesized that the compositions inside the aluminum tubes experience more preheating than those in stainless steel tubes, therefore enhancing reactivity by transmitting heat to unburned layers more effectively. In the stainless steel tubes, more of the thermal energy is confined to the composition, with less propagating through the tube walls. The burn times in these tubes are therefore longer. It is also

possible that the rapid heating of the aluminum tubes, in contrast to the stainless steel tubes, may have contributed to the black powder output charges igniting earlier. It is very clear that more work needs to be done to understand the mechanism(s) of how these particular delays function and understand the thermal heat flow characteristics of different tube configurations. Additional experiments are planned that will evaluate the effect of different input and output charges, different tube geometries (with different lengths and wall thicknesses), and different tube materials.

## Conclusions

Altering the $Bi_2O_3/Sb_2O_3$ ratio in the $Si/Bi_2O_3/Sb_2O_3$ system has been demonstrated as a viable means of varying burn rate. Inverse burn rates ranging from 0.54-1.82 s/cm (in aluminum) and 0.68-2.25 s/cm (in stainless steel) were measured in small tubes. Major differences in burn rates were observed between samples pressed in aluminum and stainless steel tubes. This was attributed to differences in the thermal effusivity and thermal diffusivity of aluminum and stainless steel, which changed the reaction front heat loss and ultimately influenced the degree of sample preheating. It is reasoned that the columns pressed in aluminum tubes were preheated to a greater degree than those in stainless steel, which enhanced the reactivity and resulted in faster burn rates.

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